



# Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid

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# Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid

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## Abstract

Freshly formed atmospheric aerosol particles are neither large enough to efficiently scatter incoming solar radiation nor able to act as cloud condensation nuclei. As the particles grow larger, their hygroscopicity determines the limiting size after which they are important in both of the aforementioned processes. The condensing species resulting in growth alter the hygroscopicity of the particles. We have measured hygroscopic growth of aerosol particles present in a boreal forest, along with the very hygroscopic atmospheric trace gas sulfuric acid. The focus was on days with new particle formation by nucleation. The measured hygroscopic growth factors (GF) correlated positively with gaseous phase sulfuric acid concentrations. This correlation had a strong size dependency; the smaller the particle, the more condensing sulfuric acid is bound to alter the GF due to initially smaller mass. In addition, water uptake of nucleation mode particles was monitored during new particle formation events and followed during their growth to Aitken mode sizes. As the modal diameter increased, the solubility of the particles decreased. This indicated that initially more hygroscopic particles transformed into less hygroscopic or even hydrophobic particles. A similar behavior was seen also during days with no particle formation, with GF decreasing during the evenings and increasing during early morning. This can be tentatively explained by day- and nighttime differences in the hygroscopicity of condensable vapors.

## 1 Introduction

Recent studies have shown that formation of new particles occurs frequently in the atmosphere (Kulmala et al., 2004). These particles grow further by coagulation and condensation. Sometimes newly formed particles grow to sizes that are relevant for scattering light or acting as cloud condensation nuclei. Due to the ubiquitous presence of particles formed via atmospheric nucleation, they are likely to be important in climate and air pollution issues.

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In order to quantitatively understand the formation and growth of new particles in atmosphere, the chemical composition of individual particles of about 1 nm and larger should be determined. However, determination of the composition of the smallest particles (<20 nm) remains tedious due to the small masses involved. The first direct measurements of the composition have been reported during recent years (Smith et al., 2004, 2005), using mass spectrometry. More characterization studies of sub-20 nm particles have, however, utilized indirect measurement methods such as determination of particle volatility and hygroscopicity (Wehner et al., 2005; Sakurai et al., 2005; Väkevä et al., 2002).

Early observations of formation and growth of new particles were made in a boreal forest research station in southern Finland (Mäkelä et al., 1997). The measurements now cover about 10 years of continuous observations of atmospheric particle formation events. However, one of the open questions is still the exact composition and formation mechanism of freshly nucleated particles. One of the early attempts to study the composition of these particles in the boreal forest was done by Hämeri et al. (2001). They measured the hygroscopicity of nucleation, Aitken and accumulation mode particles and observed a clear diurnal variation during days with particle formation. Hygroscopic growth was high during daytime and lower during nighttime. This behavior was most prominent for the smaller particle sizes, but could also be discerned for accumulation mode particles. In addition, they observed that the nighttime minimum was lower before days with new particle formation compared to days without nucleation. Differences in condensable vapor concentrations and properties were deemed to be the reason for both observations.

In this study we present focused measurements of the hygroscopicity of nucleation and Aitken mode aerosol particles together with atmospheric sulfuric acid concentrations using a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) and a Chemical Ionization Mass Spectrometer (CIMS). The measurements were conducted in a boreal forest area in Southern Finland during April and May 2005. The diurnal variation during days with and without new particle formation was analyzed. In addition, the

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influence of gaseous sulfuric acid on particle hygroscopicity was determined. Finally, the evolution of the solubility of newly formed particles was studied during their growth in order to determine changes in condensing vapor properties.

## 2 Experimental setup

5 Measurements were conducted at SMEAR II (Station for measuring Forest Ecosystem-  
Atmosphere Relations) located in Hyytiälä, Southern Finland. The site is surrounded by  
40-year-old pine forest (*Pinus Sylvestris* L.). Detailed information about the continuous  
measurements and the infrastructure can be found elsewhere ([Vesala et al., 1998](#);  
10 [Kulmala et al., 2001b](#)). This study was conducted as a part of the BACCI/QUEST-  
campaign.

### 2.1 Aerosol instrumentation

#### 2.1.1 Hygroscopicity

A HTDMA ([Rader and McMurry, 1986](#)) was used to measure hygroscopicity of selected  
nucleation and Aitken mode particle sizes. The growth was monitored at 88% for 10,  
15 20, 30 and 50 nm particles. A growth spectrum was measured in just below 10 min,  
resulting in one growth measurement for each dry size roughly every 40 min.

A schematic diagram of the HTDMA is shown in Fig. 1. The sample we wish to study  
is passed through a charger where aerosol particles experience electrical charging  
via uptake of ions formed by air ionization by a radioactive source (Ni-63; 370 MBq).  
20 Particles reach charge equilibrium before they continue into the Differential Mobility  
Analyzer (DMA). A DMA ([Winklmayr et al., 1991](#)) classifies particles based on their  
electrical mobility and is used to select a narrow size range from the polydisperse sam-  
ple. The sheath air coming into the first DMA (10.9 cm long, denoted DMA1) is dried  
and therefore possible water in the particles evaporates very quickly once it enters the

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DMA. During the measurement period, the average ambient temperature was well below 20°C, leading to a partial drying of the sample already when taken from a colder environment to room temperature. The time for particles of the measured sizes to reach equilibrium with the surrounding water vapor is less than one millisecond (Kerminen, 1997). After DMA1 we have a dry, largely monodisperse aerosol of a selected size (referred to as the dry size). We then pre-humidify the aerosol to a chosen relative humidity (*RH*), usually between 70 and 85%. The particles enter the second DMA (28 cm long, denoted DMA2) and come in contact with the humidified sheath air and reach their final humidity. At this point some of the particles may have absorbed water from the surrounding water vapor and grown to larger sizes. The humidified size distribution is scanned by counting the number of particles of different sizes passing through DMA2 to the TSI 3010 condensation particle counter (CPC, McMurry, 2000). The final particle size distribution depends on the composition of the selected particles.

The humidifiers consist of 6 mm stainless steel tube that has been cut and separated for up to 3 cm. This part has been replaced by a GoreTex-membrane, and the tubing is surrounded by liquid water. The sample flows through the tubing and is humidified by water vapor diffusing through the GoreTex-membrane. The amount of diffusing water vapor depends on the temperature of the water, so the resulting *RH* can be controlled by controlling the temperature of the water. The aerosol flow into, and the excess flow out of, DMA2 are *RH*-controlled. Both *RH*s are measured by Vaisala HMP143A humidity probes. Similarly, the sheath flow into DMA2 is measured by a HMP143A, and the excess flow out of DMA1 with a Vaisala Humitter 50Y to ensure sufficient drying of the sample flow. The excess flow out of DMA2 also contains a General Eastern Hygro M4 dewpoint sensor.

Both DMAs have closed loop arrangements (Jokinen and Mäkelä, 1997), meaning that the excess flows are filtered and reused in the sheath flow. This removes the need for pressurized air and vacuum, which might not always be available during field measurements. As the humid excess air of DMA2 is recirculated, the sheath air humidifier only adds a small amount of water vapor to the flow, thereby decreasing the water

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consumption of the system significantly. The critical orifices keep the flows very stable and no mass flow controllers are needed. Flow stabilizers (5 l plastic bottles) are used to remove the flow oscillations generated by the pumps. In the DMA1-loop the bottle is filled with silica gel to keep the flow dry, and in the DMA2-loop it is filled with glass marbles ( $d=7$  mm).

Critical orifices controlled the flows, which were measured each day. In the case of a change in one of the sheath flows, the new values were fed into the program. Both flows were close to 12 LPM and fairly stable. The aerosol/sample flow was 1 LPM. Calibration measurements with ammonium sulfate were performed daily.

## 2.1.2 Aerosol size distribution

The particle number distribution from 3 to 1000 nm was measured with a twin Differential Mobility Particle Sizer (DMPS) that has been used for continuous measurements in Hyytiälä since 1996 (Aalto et al., 2001). The twin-DMPS consists of two separate DMPS-systems measuring in parallel. The first one is optimized for small particles and has a short (10.9 cm) DMA with high flowrate and a TSI 3025 CPC. The second system has a medium-sized (28.0 cm) DMA and a TSI 3010 CPC for better counting statistics. The first system measures particles between 3 and 40 nm s and the second between 10 and 1000 nm.

## 2.2 Gaseous phase measurements

The Max Planck Institute for Nuclear Physics in Heidelberg, Germany, measured the number concentration of gaseous sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with a mass spectrometer.

The Quadrupole Ion Trap (QIT) -CIMS measured ultra-trace gases with sub-pptv concentrations. A radioactive Po-210 ion source produces the reagent ions  $\text{NO}_3^-$  and  $\text{NO}_3^-(\text{HNO}_3)$  from  $\text{NO}_2$  and  $\text{HNO}_3$ . These ions react with  $\text{H}_2\text{SO}_4$  in a flow-tube reactor at ambient pressure forming  $\text{HSO}_4^-$  and  $\text{HSO}_4^-(\text{HNO}_3)$  with rate coefficients close to the ion-molecule collision rate coefficients. Finally, an ion trap mass spectrometer is used

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to detect and identify the ions. Careful calibrations were performed using a H<sub>2</sub>SO<sub>4</sub> source based on water vapor photolysis. The detection limit of H<sub>2</sub>SO<sub>4</sub> is as low as 2×10<sup>5</sup> cm<sup>-3</sup> corresponding to an atmospheric mole fraction of 8 ppqv. The time resolution of the H<sub>2</sub>SO<sub>4</sub> measurements is better than 10 s, but usually the H<sub>2</sub>SO<sub>4</sub> concentrations were integrated over 200 s to reduce statistical error. The absolute uncertainty is ±30%. For more details, see Aufmhoff et al. (2006)<sup>1</sup>.

### 3 Data analysis

The measured particle dry sizes were 10, 20, 30 and 50 nm. Statistically sufficient concentrations of 10 nm particles were only observed during new particle formation, and therefore this data is not used in all calculations. A lower limit for the total concentration during each measurement was set for the larger particle sizes as well. The final *RH* value assigned to a scan was the average of the two sensors in the excess flow of DMA2. Measurements not between 87 and 89% *RH* were discarded.

#### 3.1 Hygroscopicity

The humidified spectra measured with the HTDMA was inverted by taking into account the transfer functions of DMA2 in accordance with [Stolzenburg \(1988\)](#). The humidified spectra measured by the HTDMA were almost without exception monomodal. At times the spectrum showed a broadening that might imply external mixing, and during a few periods a small fraction of the particles formed a separate mode. These occasions were, however, so rare that the entire dataset was analyzed as if there was only one type of particles in the air. External mixing is usually more important for larger particle sizes ([Hämeri et al., 2001](#)). The values used in the analysis are the diameter growth

<sup>1</sup>Aufmhoff, H., Hanke, M., and Arnold, F.: Atmospheric measurements of gaseous sulfuric acid: Deployment of a novel ion trap CIMS instrument, in preparation, 2006.

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factors

$$GF = \frac{\text{mean humidified diameter}}{\text{mean dry diameter}}. \quad (1)$$

Each measurement is therefore described by a single value, the GF.

Determination of the correct *RH* inside DMA2 is the most significant source of uncertainty in the measurements. We are not able to measure the temperature inside the DMA, and therefore we can not determine the precise relative humidity. A deviation of 0.3 degrees between the DMA and the measurement probe in the excess flow would lead to an error of 1 percentage point in *RH*. The uncertainty of the measurements was estimated to a change in GF of  $\pm 0.05$ .

### 3.2 Particle soluble fractions

A simplified two-component model was applied to the hygroscopic data as suggested by Swietlicki et al. (1999). The model assumes that a particle consists of a hydrophobic component that is insoluble, and a soluble compound that absorbs water independently of the inert component. Assuming further that the soluble compound is ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), we can calculate the fraction of soluble material in the particle. The hygroscopic behavior of ammonium sulfate is known fairly accurately due to many experimental and theoretical studies on the thermodynamics of water – ammonium sulfate particles. This soluble fraction  $\epsilon$  is therefore given by

$$\epsilon = \frac{GF_{\text{amb}}^3 - 1}{GF_{\text{AS}}^3 (D_p) - 1}, \quad (2)$$

where GF<sub>amb</sub> is the measured GF of the particle and GF<sub>AS</sub> is the GF of a pure ammonium sulfate particle that has grown to the size of the measured particle (*D<sub>p</sub>*). In our calculations of the GF of water-ammonium sulfate particles, we have used the polynomial fit for the molality from Potukuchi and Wexler (1995) and the density fit from Tang and Munkelwitz (1994). When calculating the Kelvin effect we have used the

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surface tension fit by [Korhonen et al. \(1998\)](#). This two-component model was used to investigate the change in soluble fractions of recently formed particles during their growth.

If the mean  $RH$  during a measurement was not exactly at the setpoint, the GF was scaled to this value by using the above mentioned model: the soluble fraction was calculated at the measured  $RH$ , and thereafter the growth factor at the setpoint- $RH$  was evaluated.

The twin-DMPS system measured the time evolution of the size distribution. Based on this data, days were selected keeping in mind several criteria: new particle formation was detected and the particles formed a clear mode, the particles grew without distinct interruptions due to the change of air mass, and concurrent hygroscopicity measurements were available.

To characterize the temporal evolution of the mode of new particles, log-normal distributions were fitted to the DMPS data ([Hussein et al., 2005](#)) to obtain the position, width and size of the mode of new particles. The position was expressed as the geometric mean diameter (GMD) and the width by the standard deviation ( $\sigma$ ). This gave us a measure of the distance between the GMD of new particles and the dry size ( $D_{p,dry}$ ) measured by the HTDMA through

$$\Delta\sigma = \frac{\log(D_{p,dry}) - \log(\text{GMD})}{\log(\sigma)}. \quad (3)$$

When a HTDMA measurement was made within 5 min of a DMPS scan, and the difference between GMD and dry size was less than one standard deviation ( $|\Delta\sigma| < 1$ ), the soluble fraction was calculated.

This two-component model can also be used to determine the amount of insoluble and soluble gases condensing onto the particles and causing them to grow ([Kulmala et al., 2001a](#)). When we know the soluble fractions at two different sizes, we can calculate the ratio of insoluble to soluble gas flux (denoted  $I_1$  and  $I_2$ , respectively) onto the particles. This gives an indication of the change in condensing vapors during the

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different stages of the growth.

## 4 Results and discussion

HTDMA measurements were conducted 1 April through 18 May 2005. During this time new particle formation events were observed during 1, 3–6, 12–14, 16–20, 24–27, 30 April and 2, 3, 7, 11–14, 16 May. Henceforth, these days will be referred to as “event days”. An example of an event day is plotted in Fig. 2, containing the size distribution and particle number concentration measured by the DMPS, gaseous sulfuric acid concentration measured by the CIMS, and the solar (global) radiation measured at a height of 18 m with a Astrodata Reemann TP3 pyranometer.

### 4.1 Diurnal variation of hygroscopicity

During the campaign the growth factors varied from day to day, but a clear diurnal cycle was present during a single day, namely higher growth factors during daytime than nighttime. This phenomenon has been observed previously in Hyytiälä by Hämeri et al. (2001) during event days. Their study showed that the effect is strongest for ultrafine particles, but can also be observed for larger particles.

We divided the measurements between days with and without events and averaged the hygroscopicity data over three-hour periods sacrificing some resolution for better statistics. Figure 3 shows the results for 20, 30 and 50 nm particles. There is an increase in the growth factors of about 0.1 during non-event days and about 0.15 during event days compared to the corresponding nighttime values. A diurnal variation can, in other words, be detected both during days with, and days without particle formation. This diurnal variation can result from the different atmospheric conditions during day and night. For example  $\text{H}_2\text{SO}_4$ , which has a high water vapor affinity, correlates with global radiation (Fig. 2) and usually reaches maximum gas-phase concentration around noon (Boy et al., 2005; Fiedler et al., 2005) whereas many organic compounds with low

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hygroscopic GF (Virkkula et al., 1999) have maxima during the night (Sellegrì et al., 2005). The condensation of these gases onto the particles will alter the hygroscopicity of the particles. This effect will be strongest for small particles and less noticeable for larger ones.

5 The GF is clearly lower during a night before a nucleation event for all sizes, and during the morning the GF rises quickly and reached its maximum some time after noon. The highest growth factors were measured for 30 nm and the lowest for 50 nm particles. During non-event days the GF of 20 nm particles is well below the larger sizes, which, in turn, show very similar behavior. The hygroscopicity of 20 nm particles  
10 therefore increases a significant amount during an event day, 30 nm particles increase slightly whereas the hygroscopicity of 50 nm particles decreases, compared to a non-event day. This is a surprising result, since condensation of hygroscopic gases onto the particles is thought to be the reason for the increase in GF, but this would also lead to an increase in the GF of 50 nm particles. There were large variations between different  
15 days, so the decrease may be due to insufficient statistics.

The growth factors during the nights after event days compared to those after non-event days are higher for 20 nm, similar for 30 nm and smaller for 50 nm particles. This indicates that the effects of a nucleation event continues past midnight, and we should therefore not limit our analysis to only one day. Figure 4 constitutes a good example of  
20 an event that clearly effects the particle size distribution of the following day. The figure shows DMPS-data for the 6 and 7 April with a large amount of new particles forming during the first day. The mode of new particles grows, and only just before midnight does it reach 50 nm.

25 Studying each day separately, we only have to distinguish between days with and without events. When extending our analysis to two days, the number of different possibilities double. The four combinations are (day 1/day 2): event/event, non-event/event, event/non-event and non-event/non-event. Figure 5 shows the corresponding analysis for 50 nm particles with the GF:s again averaged over three hours. Each plot in Fig. 5 is a mean of between 9 and 15 two-day periods, so the statistics are limited. Note that

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each day of the campaign, except the first and the last, will be counted once as “day 1” and once as “day 2”. The most interesting period in the figure is the time between evening of day 1 and evening of day 2. We observe very low GF:s (below 1.15) during the previous night if day 2 is an event day (red and blue lines), independent of whether the day before was an event day or not. On the other hand, when day 2 is a non-event day, a dependency on the previous day is clear. The non-event/non-event combination (black line) can be thought of as the hygroscopic behavior of the “background” particles in the forest increasing from about 1.18 during the night to about 1.28 during the day. The green plot corresponds to the situation shown in Fig. 4 with particles forming during day 1 and possibly reaching 50 nm during the evening or night. For these particles the minimum occurs before midnight, about six hours before all the other cases. The nightly minimum (just above 1.20) and the maximum during day 2 (about 1.32) are also the highest of the four cases. The highest nightly minimum for 20 and 30 nm particles were found during event/non-event days as well, and the day 2 maximum was very close to those during event/event days.

Event days were preceded by lower GF than non-event days. This would imply that conditions favorable for particle formation events can be seen already during the previous night and morning. The nucleating/condensing vapors might already be present and condensing on the pre-existing particles. On the other hand, low GF also means a lower condensation sink, which in turn makes nucleation more probable. The decrease in pre-existing particle area due to the observed difference in GF is, however, less than 10%.

## 4.2 The influence of $\text{H}_2\text{SO}_4$ on aerosol hygroscopicity

The MPI in Heidelberg measured the amount of  $\text{H}_2\text{SO}_4$  in the gas-phase during the campaign and the results were compared to the hygroscopic data measured with the HTDMA. For the comparison we discarded all  $\text{H}_2\text{SO}_4$  data where the uncertainty limits were higher than the concentration itself, and all hygroscopicity data where the particle counts were too low for statistically reliable results. Only measurements done during

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the day (06:00–18:00) were included, due to the low nighttime  $\text{H}_2\text{SO}_4$  concentrations. All  $\text{H}_2\text{SO}_4$  acid measurements done within ten minutes of a HTDMA scan were averaged and compared to the measured growth factor. The results are plotted in Fig. 6. The x-axis is logarithmic due to the large variation in  $\text{H}_2\text{SO}_4$  concentrations (values between  $10^5$  and  $3 \times 10^7$ ). Each dot corresponds to a HTDMA measurement and the red line is a linear fit to the data. Since the line is not drawn straight due to the log-linear scale, the equation for each line is written in the bottom right corner of the graphs together with the correlation coefficient between  $\text{H}_2\text{SO}_4$  concentrations and GF. Both the correlation coefficient and the steepness of the line increase when the particle size decreases. Even though the correlation is smaller for the larger sizes, when looking at  $\text{H}_2\text{SO}_4$  concentrations above  $10^7 \text{ cm}^{-3}$ , the growth factors are clearly higher than on average.

If we limit the analysis to days with new particle formation, all correlation coefficients increase, since these days usually have higher sulfuric acid concentrations than days without particle formation. The largest change is observed for 50 nm particles, with the correlation coefficient doubling and the steepness of the line increasing by about 60%. For 20 and 30 nm particles, the changes are smaller, but noticeable. 10 nm particles are usually only observed during particle formation and therefore the changes to these particles are marginal.

$\text{H}_2\text{SO}_4$  has a low saturation vapor pressure and is very water soluble. The stronger effect of  $\text{H}_2\text{SO}_4$  on small particles was to be expected since these particles have less mass and therefore small amounts of condensing vapor have a larger effect on their composition.

#### 4.3 Soluble fractions during particle growth

We selected 9 days (3, 6, 12, 13, 27, 30 April and 2, 12, 13 May) with new particle formation for closer investigation. The days were chosen based on the quality of the HTDMA data and the duration of the particle formation event. Event days with unclear modes or clearly changing air masses were discarded. Contour plots of particle size

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distributions measured with the twin-DMPs for the selected days are shown in Fig. 7. There are clear differences between the days, both in amounts and in growth rates of the new particles.

The soluble fractions are plotted in Fig. 8. The purple curve shows the position (GMD) of the mode, and the markers the soluble fractions at that time. The different colors correspond to different dry sizes in the HTDMA, and the symbols the relative position of the mode compared to the dry size.

The large variation in soluble fractions for 10 nm particles shows that there may be very different compounds, or ratios between the compounds, involved in the initial growth of new particles. During 27 April, the soluble fractions are above 1, implying that the particles contain material more hygroscopic than ammonium sulfate. We can also note the interesting fact that events that start with particles with low soluble fractions (3 April, 6 April, 12 May and 13 May) tend to continue for a longer time and result in larger particles than events which start with higher soluble fractions. Due to the small amount of days studied, no further going conclusions can as yet be drawn from this.

The soluble fractions were always highest for the 10 nm particles. The maximum in soluble fractions was usually observed during the day, and after about 16:00 it started decreasing. During the days when we were able to follow the mode of new particles long enough, we saw that the soluble fraction stopped decreasing and evened out around midnight at a value close to 0.2. The growth rate of the modes were far from constant, and at times the size of the modes even decreased, as seen most clearly during the last day.

For some more concrete values of the soluble fractions during different stages of particle growth, see Table 1. These are soluble fractions from the measurements closest in time to when the mode passed a dry size measured by the HTDMA. Columns 2–5 show the soluble fractions of the particle sizes during the different days with an average value calculated for each size. Dash (–) indicates that the mode never reached the specified size. The mean values clearly show how the soluble fraction decreased as the particle size increased. Columns 6–9 give the ratio of insoluble ( $I_1$ ) to soluble

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( $I_2$ ) gases condensing on the particles when growing from 10 to 20, 20 to 30, and 30 to 50 nm. For the growth from 10 to 20 nm we found values between 0.19 and 1.64 with a mean of 0.90. Earlier, Kulmala et al. (2001a) calculated values of 0.71, 0.92 and 1.4 for three case studies, which agrees well with our findings. We have ignored the values from 4 April since this was an exceptional day with the growth occurring 4–8 h later than any other day. The average ratios  $I_1/I_2$  for the growth from 20 to 30 nm and from 30 to 50 nm were 2.29 and 8.67, respectively.

The contribution of  $H_2SO_4$  to particle growth from 10 to 20 nm was calculated according to Kulmala et al. (2001a). During the studied days, it on average accounted for 14% (std=8%) of the soluble flux  $I_2$ . The contribution to the total growth from 10 to 20 nm was 8.6% which agrees well with previous measurements from Hyytiälä in 2003, when Boy et al. (2005) calculated the contribution to be 8.9% of the growth from 3 to 25 nm. This may indicate that one or more soluble organic compounds are condensing on the particles, causing them to grow.

The decrease in soluble fractions with increase in particle size may follow from the fact that the growth to larger sizes usually happens during the evening and night. As previously mentioned this may result from the diurnal differences in condensable gases. The data from columns 2–5 in Table 1 has been plotted as a function of time of day in Fig. 9. The soluble fractions of 10 and 20 nm particles (black and red markers) seem independent of when the specific size is reached. The black, red and green markers that occur the latest in Fig. 9 correspond to 6 April and form the exception to the previous. The 30 nm particles, however, have a clear dependency on the time of day, with soluble fractions decreasing with time of day.

## 5 Conclusions

A HTDMA was deployed to measure the hygroscopicity of ultra-fine particles in a boreal forest. A diurnal variation with smaller growth factors during nights was detected. The difference between night- and daytime averages was larger during days with new parti-

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cle formation. The effects of a nucleation event did not end before midnight, wherefore the analysis was extended to two consecutive days. For 50 nm particles a non-event day showed clearly higher growth factors if the previous day had been an event day.

A correlation between the amount of  $\text{H}_2\text{SO}_4$  and the GF was observed. This was most clear for 10 nm particles, for which an increase in  $\text{H}_2\text{SO}_4$  concentration from  $10^6$  to  $10^7$  would, on average, cause an increase in GF of over 0.1.

Soluble fractions were calculated for 9 days with clear particle formation. The change in soluble fractions was followed as the mode of new particles grew. The soluble fractions followed a similar pattern as the diurnal GF variation. Large differences were seen in the soluble fractions of 10 nm particles (from 0.5 to 1.1) which indicates that the mechanism producing these particles is not always the same. Different condensing vapors were likely the main reason.

Continuous HTDMA measurements have been planned in Hyytiälä, and these measurements will give a better statistical basis for further analysis of hygroscopic properties.

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**Table 1.** Soluble fractions ( $\epsilon$ ) and insoluble-to-soluble mass flux ratios ( $I_1/I_2$ ) during different stages of the particle growth. The soluble fractions usually decrease with increasing particle size due to more insoluble vapors contributing to the growth.

Day	$\epsilon_{10}$	$\epsilon_{20}$	$\epsilon_{30}$	$\epsilon_{50}$	$\left(\frac{I_1}{I_2}\right)_{10 \rightarrow 20}$	$\left(\frac{I_1}{I_2}\right)_{20 \rightarrow 30}$	$\left(\frac{I_1}{I_2}\right)_{30 \rightarrow 50}$
3.4.	0.48	0.44	0.27	–	1.31	3.94	–
6.4.	0.13	0.10	0.12	–	(9.57)	(6.45)	–
12.4.	0.69	0.50	–	–	1.13	–	–
13.4.	0.77	0.62	–	–	0.66	–	–
27.4.	1.08	0.74	–	–	0.45	–	–
30.4.	0.76	0.83	0.72	–	0.19	0.48	–
2.5.	0.86	0.76	–	–	0.33	–	–
12.5.	0.51	0.40	0.30	0.13	1.64	2.91	10.10
13.5.	0.49	0.42	0.37	0.18	1.46	1.82	7.25
Mean	0.64	0.53	0.33	0.16	0.90	2.29	8.67

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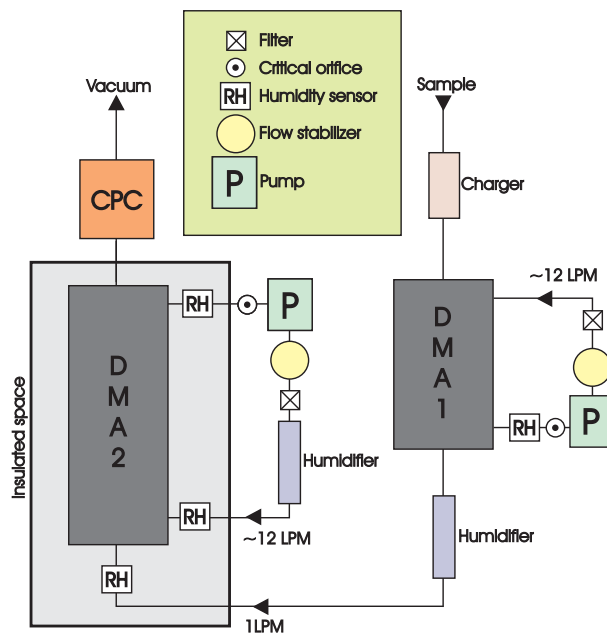
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**Fig. 1.** Schematic diagram of the HTDMA.

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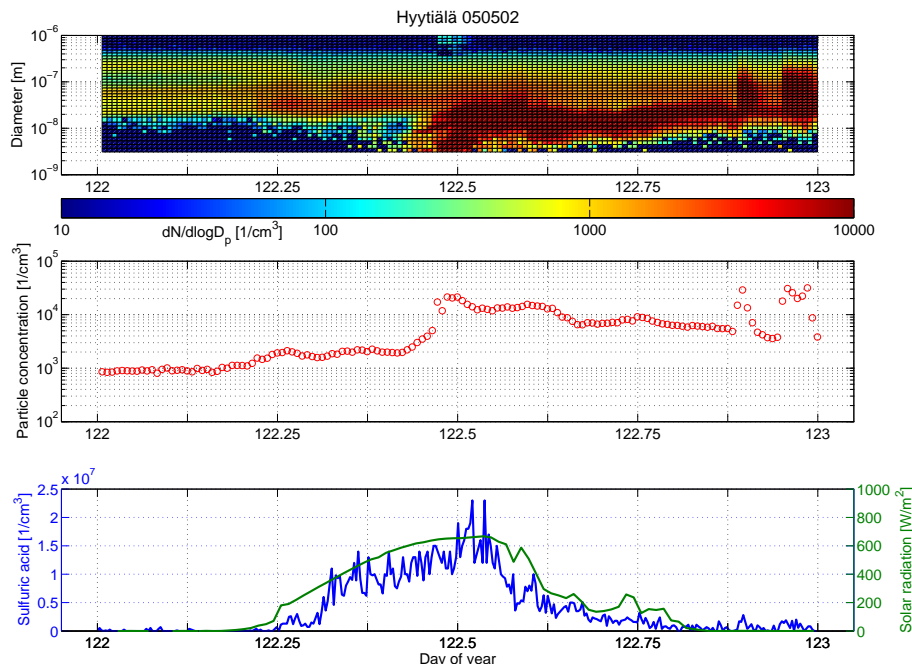
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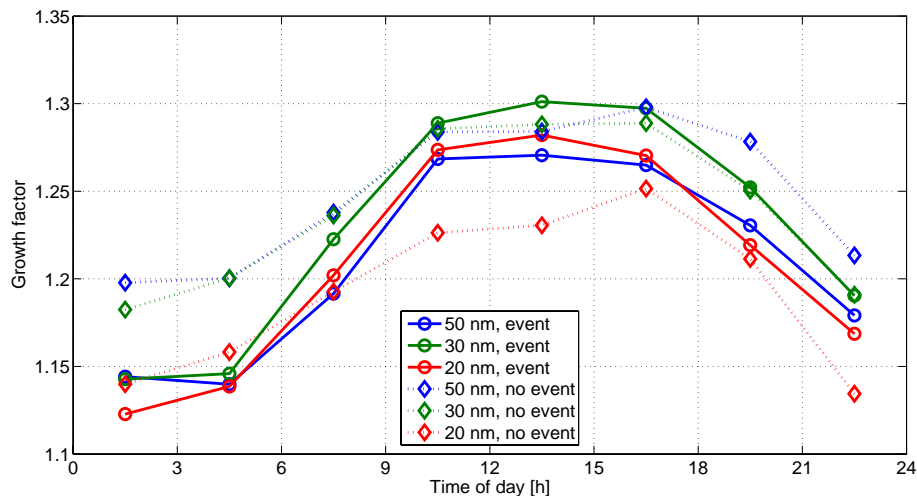


**Fig. 2.** Size distribution and sulphuric acid data for 2 May 2005. A burst of new particles is detected before noon (top panel), increasing the total particle concentration by an order of magnitude (middle panel). The bottom figure depicts the solar radiation and gaseous sulfuric acid concentration, both following a very similar pattern, peaking just after noon.

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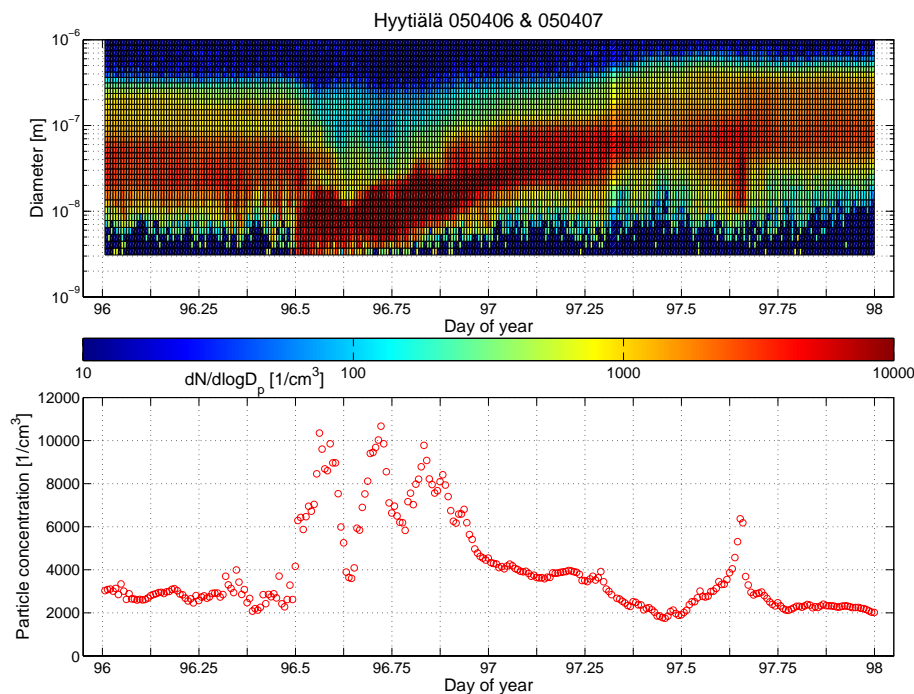
**Fig. 3.** Diurnal variation of the growth factors for 20, 30 and 50 nm particles. The data is averaged over 3 h periods. The solid and dashed lines correspond to event days and non-event days respectively. Event days are always preceded by nights with lower growth factors.

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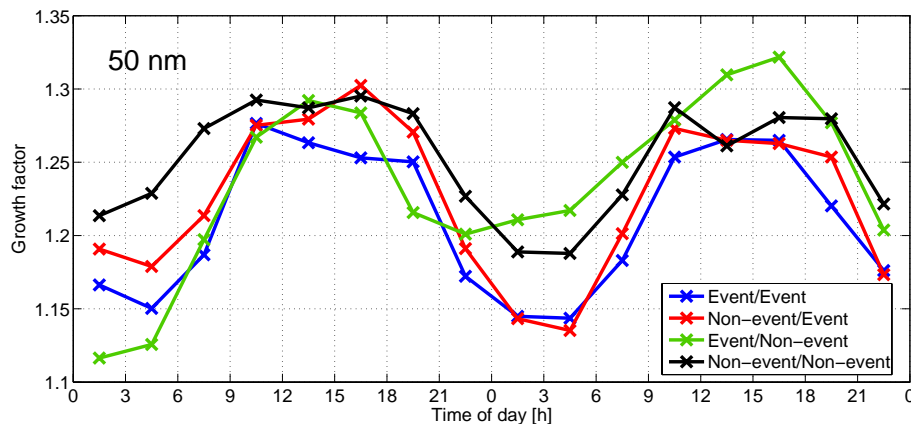


**Fig. 4.** Size distribution data for two consecutive days (6–7 April 2005). The top panel shows new particles forming during the first day and growing during the evening and night. At midnight the modal diameter has increased to 20–30 nm:s. Corresponding particle number concentrations are plotted in the bottom panel.

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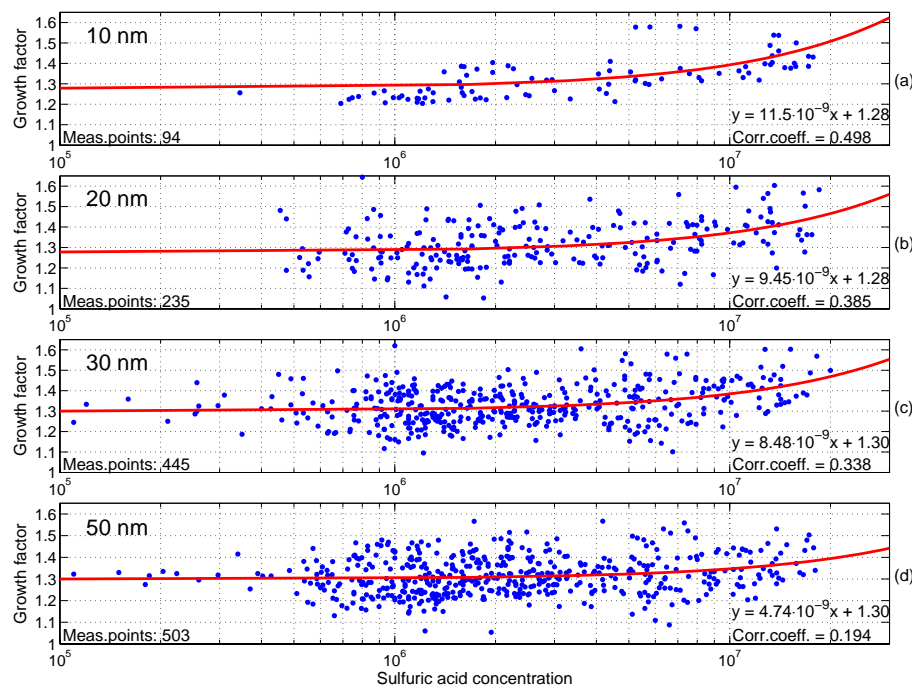


**Fig. 5.** The diurnal variation of the GF for 50 nm particles during a period of two days. The plots correspond to the four possible combinations of event days and non-event days.

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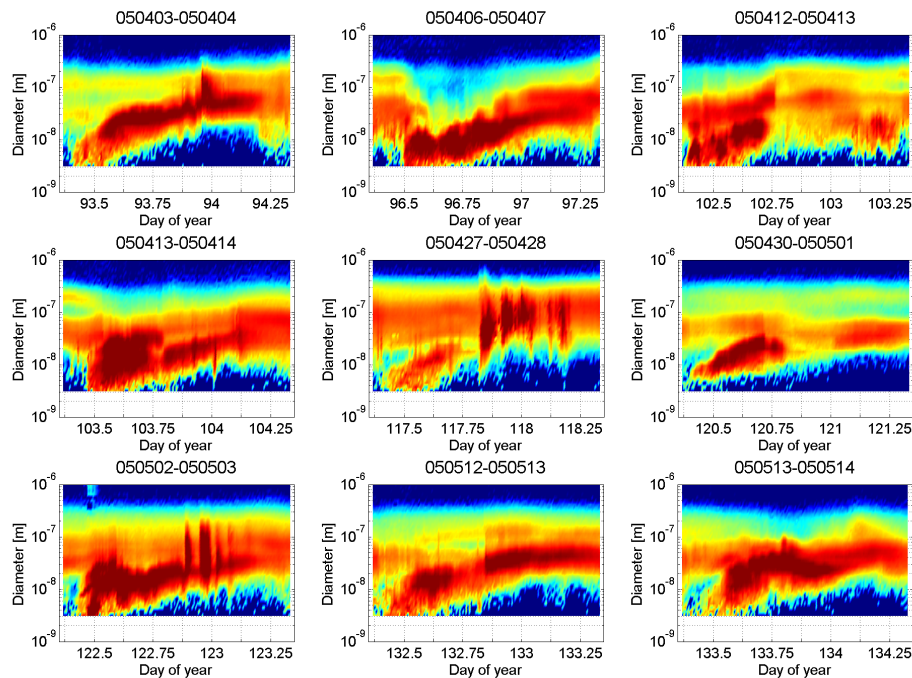


**Fig. 6.** Growth factor dependency on  $\text{H}_2\text{SO}_4$  concentration. The red line is a linear fit to the data points and indicates that the  $\text{H}_2\text{SO}_4$  concentration has a stronger effect the smaller the particles are.

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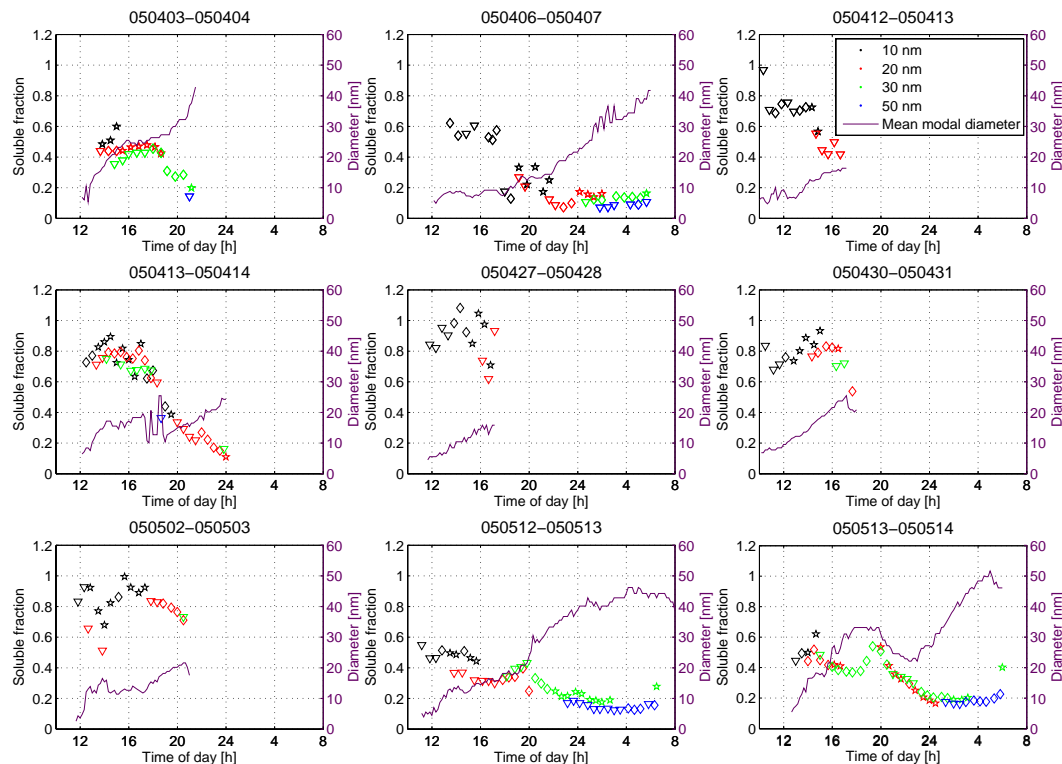


**Fig. 7.** Particle size distributions for 9 days with new particle formation.

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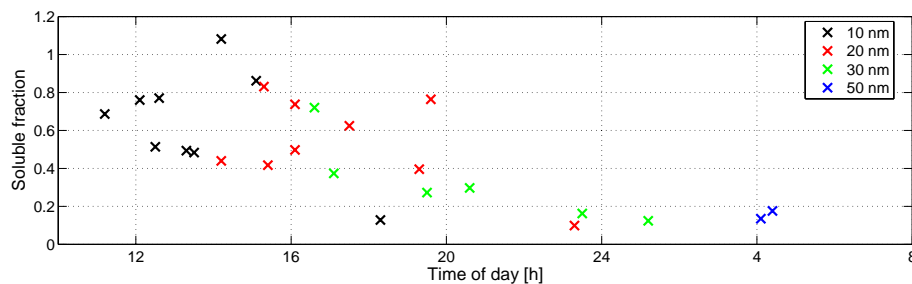


**Fig. 8.** Soluble fractions of particles during 9 days with particle formation. The purple line shows the center of the mode of new particles and each marker corresponds to the soluble fraction calculated from a single HTDMA scan. The color of the markers indicates the dry size in the HTDMA measurements and the shape the relative placement of the mode to the dry size. The triangles ( $\Delta$ ) denote  $\Delta\sigma < -0.4$ , the squares ( $\diamond$ ) that  $\Delta\sigma$  is within  $[-0.4, 0.4]$ , and the five-pointed stars ( $\star$ ) denote  $\Delta\sigma > 0.4$ .

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**Fig. 9.** Soluble fractions of new particles as a function of time. Each marker corresponds to the modes of new particles reaching 10, 20, 30 or 50 nm. The soluble fractions clearly decrease with time.

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